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STUDIES OF METHANE-OXIDATION KINETICS BY LASER AND CONVENTIONAL--ETC(U)
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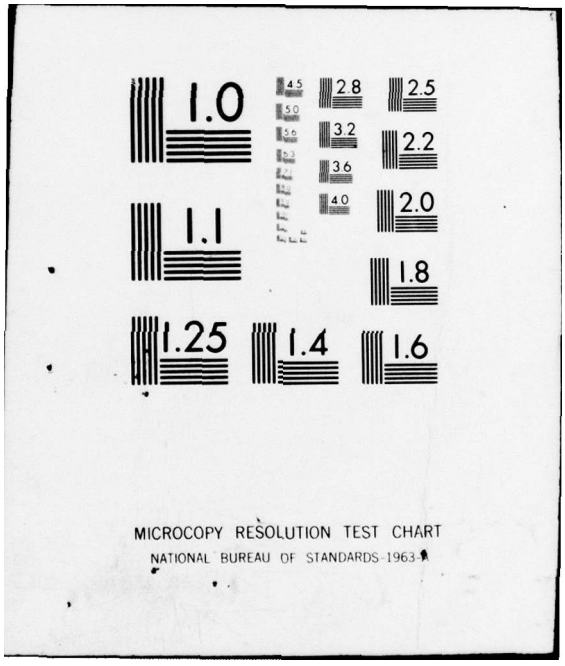
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California Univ. of La Jolla, Ca.
San Diego

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December 30, 1977

(6) (9) FINAL REPORT. (12)

Studies of Methane-Oxidation Kinetics by Laser and Conventional Spectroscopy.

ONR Contract No. (15) N00014-75-C-0261 new

In this report, we emphasize the research accomplishments of the last year of a four-year study dealing with methane-oxidation kinetics. It should thus be regarded as a supplement to the more extensive final report transmitted during December 1976.

1. Publications

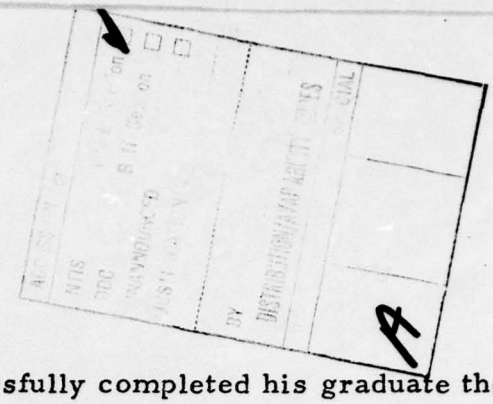
The following papers have been completed or have appeared in print during 1977:

a) "Shock-Tube Studies of Methane Pyrolysis and Oxidation Kinetics," by S. S. Penner, K. G. P. Sulzmann, W. M. Heffington, and G. E. Parks. This is a summary paper which was presented at the Vth International Combustion Symposium in Kraków, Poland, during the week of September 12. The paper will be published in the Polish Archives of Thermodynamics and Combustion during 1978 or 1979.

b) "Low-Btu Gas Mixtures. I. Methane Oxidation Rates for a Wide Range of Equivalence Ratios," by S. S. Penner, W. M. Heffington, G. E. Parks, and K. G. P. Sulzmann, Energy 2, 197-205 (1977).

c) "High-Temperature Emissivities of Complex Gas Mixtures in the 4.8 μ Region," by W. M. Heffington, G. E. Parks, K. G. P. Sulzmann, and S. S. Penner, JQSRT 18, 361-363 (1977).

d) "Equilibrium and Non-Equilibrium Radiation Observed in Shock-Tube Studies of Methane Oxidation," by S. S. Penner, K. G. P. Sulzmann, W. M. Heffington, and G. E. Parks, JQSRT (in press, 1978).



2. Personnel

W. M. Heffington successfully completed his graduate thesis research for the PhD degree in Engineering Sciences during August 1977. He has accepted an appointment as Assistant Professor at Texas A and M University. Jules M. Kline has begun studies under the ONR contract, with emphasis on reaction between CH_2O and N_2O.

3. Summary of Research Accomplishments

The high-temperature spectral absorption coefficient of methane has been measured in the range $965 \leq T, {}^\circ K \leq 2710$ behind shock waves by using an He-Ne laser as a light source at 3.392 μ. The observed temperature dependence for the absorption coefficient may be satisfactorily accounted for in terms of a simplified spectroscopic model for spherical-top molecules. The rate constant for the elementary process $CH_4 + M \rightarrow CH_3 + H + M$ was determined by using this laser-absorption technique.

Induction times and overall reaction rates in the post-induction phase have been determined in CH_4-O_2-Ar mixtures. Our induction times correlate reasonably well with earlier results below 2200°K, but are relatively smaller at higher temperatures and show the ordering $t^i_{OH} < t^i_{CH} \leq t^i_{C_2}$ for emission from electronically excited levels of OH, CH, and C_2. The observed overall methane-oxidation rates may be described in terms of bimolecular rate processes involving, for example, the fuel and oxidizer concentrations to the first power.

Equilibrium emission near 4.8 μ and in the region 3100 to 5152 A can be satisfactorily accounted for in CH_4-O_2-Ar mixtures. Near 4.8 μ, it is due to CO_2, CO and H_2O; in the region 3100 to 5152 A, CO-O and O-atom recombination radiation and the O_2 Schumann-Runge bands are the primary contributors.

Excited-state OH emission must also be allowed for near the OH-band origin. For OH, the just-overlapping line model of spectral absorption coefficients was found to be unsuitable near the band heads.

Non-LTE concentration estimates have been derived for OH^*, CH^*, and C_2^*.

An experimental procedure for mapping the complete concentration-time profiles for the chemical species that occur in a representative reaction scheme has been defined. The consistency of postulated reaction mechanisms and rates may be verified by comparisons of calculated and observed concentration-time histories. Experimental verification of this ambitious study has not yet been accomplished.

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